

Phonon in SrTiO_3 under finite electric fields

Ivan I. Naumov and Huaxiang Fu

Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

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Abstract

We propose an efficient approach within the density-functional theory to determine the phonon structure of infinite solids under finite electric fields. We apply this approach to technological SrTiO_3 , predicting many unusual properties—including a giant frequency shift, anomalous piezoelectric response, as well as striking dielectric tunability. A microscopic understanding for individual phonon modes under finite electric fields is also provided.

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It has been nearly 40 years since Worlock and Fleury discovered by means of Raman scattering that *under finite electric fields* the transverse-optical (TO) phonon in SrTiO_3 , [1] as well as in KTaO_3 , [2] exhibits a striking shift in frequency—by more than 400% of its zero-field value—when a very small field of 12 kV/cm is applied. [1] Despite its obvious importance, this giant field-induced shift of phonon frequency has not thus far been independently investigated and/or understood via the powerful density-functional theory (DFT) which, on the other hand, has been amply applied in the past three decades on a variety of *other* material properties. The reason lies in the difficulty in handling finite electric fields within the direct DFT approach, a topic that has recently drawn a great deal of interest and progress. [3, 4, 5, 6, 7, 8, 9]

SrTiO_3 is an incipient ferroelectric that is approaching, but does not in fact undergo, a paraelectric-to-ferroelectric phase transformation when lowering temperature, and is often considered as an “inert” perovskite. [10] However, being on the edge of phonon softening, SrTiO_3 shows unusual sensitivity on external electric fields that are able to drive easily the occurrence of the phase transition, and thus likely lead to an anomaly in the field-induced structural response. Given their technological importance, this and other similar ferroelectric incipients (in particular, when they are under finite electric fields) remain, nevertheless, poorly understood. For instance, it is not clear how different phonon modes may respond differently to the electric fields in terms of their frequencies and in terms of their atomic participations (that is, the phonon properties). Furthermore, little is known on how atomic displacements driven by external fields will couple with strain in incipients (i.e., the mechanical properties), and whether SrTiO_3 in *finite* electric fields can be a good piezoelectric, in addition to being a good dielectric. Finally, a direct DFT modelling of the “dielectric tunability” by finite electric fields in incipients (i.e., the dielectric properties) is still at its early stage and thus much needed. [11]

The purpose of this Letter is threefold: (1) to show that it is possible to devise a direct density-functional approach to determine and understand the phonon spectrum of infinite solids under finite electric fields; (2) to demonstrate that the approach works robust for incipient SrTiO_3 , and in particular, the theoretical prediction of field-induced frequency shift is in excellent agreement with the result observed in experiments; (3) to present other unusual properties in SrTiO_3 that occur “only” under finite electric fields, that is, a gigantic piezoelectric response as well as a superior field-induced dielectric tunability.

To determine phonon structure, namely vibration frequencies and phonon eigenmodes, of a solid under finite electric fields, we start with free energy $F = U - \mathbf{E} \cdot \mathbf{P}$, where \mathbf{E} (assumed here to be along the pseudo-cubic [001] direction) and \mathbf{P} are the screened macroscopic field and polarization per cell, respectively. This yields force-constant matrix elements as

$$\frac{\partial^2 F}{\partial r_{i\alpha} \partial r_{j\beta}} = \frac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}} - E \frac{\partial Z_{3\alpha}^*(i)}{\partial r_{j\beta}}, \quad (1)$$

where $r_{i\alpha}$ is the position of atom i along the α cartesian direction, and $Z^*(i)$ is the Born effective charge tensor of this atom. It should be emphasized that each term in the right-hand side of Eq.(1) must be evaluated at *field-induced* new atomic-positions $\{\mathbf{R}_{\text{new}}\}$ and cell-shape strain $\{\eta_{\text{new}}\}$, instead of the zero-field $\{\mathbf{R}_0\}$ and $\{\eta_0\}$.

Determination of the force-constant matrix of Eq.(1) is done in two steps. First, $\{\mathbf{R}_{\text{new}}\}$ and $\{\eta_{\text{new}}\}$ are obtained using a newly-developed method that was described in Ref. 12. Second, the force-constant matrix is evaluated as follow. The first term in Eq.(1), which is associated with the *zero-field* internal energy U but at displaced atomic positions, is ready to be computed using standard density-functional perturbation theory (DFPT).[13, 14] The second term requires, however, a perturbation theory of the macroscopic polarization \mathbf{P} with respect to the atomic displacements, and is rather cumbersome to deal within the DFPT. Here, we numerically find (by performing finite-difference calculations) that, even for an electric field as large as 0.5×10^8 V/m, the second term in Eq.(1) turns out to be less than 0.5% of the first term for all diagonal elements, and thus *contributes practically very little to the dynamic matrix*. This particular finding allows us to neglect the insignificant second term. The resulting simplicity and efficiency in the present approach is precisely what we pursue, and allows the determination of the phonon structure under finite electric fields to be routinely performed within the DFT. This approach works in general for phonon at any wave-vector \mathbf{q} , whereas in the following we focus on the phonon modes at the zone center since they can be directly compared with Raman experiments.[1, 2]

It should be pointed out that, apart from the (externally-applied) field \mathbf{E} , a long-wavelength longitudinal-optical (LO) phonon in polar materials will generate a second macroscopic field \mathbf{E}_1 with its direction depending on the phonon wave-vector \mathbf{q} . Here we choose to study a configuration that likely leads to most pronounced effects that are to be caused by the applied field \mathbf{E} , namely, when \mathbf{E} and \mathbf{q} are *perpendicular*, with \mathbf{q} chosen along the pseudo-cubic [010] direction.

Obviously, quantum fluctuation effects in SrTiO₃ at low temperature, which are responsible for its incipient behavior, can not be described by zero-temperature DFT calculations and are not the focus of this work. On the other hand, the DFT is able to predict quantitatively the electric-field effects in SrTiO₃, since these effects are mainly determined by the zero-field frequency (i.e., the energy surface) of the ongoing soft mode (assuming that this frequency is correctly reproduced by DFT). Furthermore, anti-ferroelectric rotation in low-temperature SrTiO₃ is not considered here, as it affects mainly the zone-boundary (not the zone-center) phonons.

Technically, our calculations are carried out using the ABINIT code,[15] modified to perform *finite-field* geometry optimization. A sufficient energy cutoff of 110 Ry is used to ensure a satisfactory convergence. The zero-field lowest TO phonon, that turns soft in *normal* ferroelectrics, is found to be still stable and at the frequency of 13.2 cm⁻¹ for cubic SrTiO₃ with the lattice constant 3.892 Å. This frequency is in good agreement with experimental value of 11 cm⁻¹[1], and in fact, an agreement is found for all modes across the phonon spectrum.

Fig.1 shows the phonon spectrum under an electric field of 0.22×10⁸ V/m, compared to the zero-field case. The most striking results are: (1) Upon the electric field, the degeneracy is completely lifted for all phonon modes, and in particular, for the zero-field “silent” modes (being triply-degenerate with Γ_{25} symmetry in cubic SrTiO₃). Being *non-polar* with only oxygen amplitude, these silent modes were commonly thought to split into one singlet and one doublet by electric fields [16]. (2) The lowest two modes in the lower panel of Fig.1, which split from a doublet TO phonon in the upper panel, undergo *giant* shifts in frequency from 13.2 cm⁻¹ at zero field to 48.7 and 92.2 cm⁻¹ at the considered magnitude of field. In other words, the frequencies of these modes are altered by the applied electric field by more than 400% and 800% (!), respectively. (3) Another mode at zero-field frequency of 163.2 cm⁻¹ (notice that this is *not* the ongoing soft mode) displays also a remarkable frequency shift by as much as 26.6 cm⁻¹. (4) On the other hand, modes at 447.0 and 772.4 cm⁻¹ are found to be *least* affected (if any).

In order to understand the *microscopic* origin of why some modes, not others, are drastically altered by electric fields, and furthermore, to provide valuable guide for understanding future experimental results, Table I gives the vibration eigenvectors of the phonon modes. Surprisingly, the second mode in this Table—namely, the mode displaying the largest field-

induced frequency shift, vibrating in parallel with the \mathbf{E} direction, and its frequency to be referred to as ω_{\parallel} —turns out to have *virtually no* amplitude from Ti, instead it is predominantly from strontium and oxygen atoms. This is in contrast with the zero-field situation where Ti contribution is large (~ 0.31) for the corresponding mode. On the other hand, another (also z -axis polarized) mode at 189.8 cm^{-1} shows an opposite trait, with a *heavy* Ti involvement. Also interestingly, it can be seen in Table I that a large field-induced frequency shift occurs not only to those modes that vibrate *parallel* to \mathbf{E} , as it should (for instance, see the modes at 92.2 , 189.8 , and 549.9 cm^{-1})—and in fact, the applied field also produces a remarkable shift to the mode that is *transverse* to the field direction (see, the first mode in Table I, and the frequency of this mode will be denoted as ω_{\perp} hereafter). Meanwhile, the modes that exhibit the least frequency shift (e.g., modes at 447.0 cm^{-1} and at 772.4 cm^{-1}) are found to associate with vibrations along the $[010]$ direction. This can be explained by the fact that these modes originate from the \mathbf{E}_1 field due to the LO/TO splitting and thus subject to little effects from the applied \mathbf{E} field.

We now wonder how the phonon frequencies may vary with different field-strengths, and the results are depicted in Fig.2a for the ω_{\parallel} and ω_{\perp} modes. Intriguingly, our results show that the field-induced increase in frequency (i.e., so-called “phonon hardening”) is characterized by two drastically different regimes, separated by a critical field E_c and equal to $\sim 0.5 \times 10^8 \text{ V/m}$. Below E_c , ω_{\parallel} and ω_{\perp} increase *dramatically* and strong *nonlinearly*—with their difference $\omega_{\parallel} - \omega_{\perp}$ first enlarged and then saturated at E_c —as the field strength increases. On the other hand and above E_c , ω_{\parallel} and ω_{\perp} show almost a *linear* field-dependence, and interestingly, the frequency-vs-field slopes are nearly equal for these two modes, whereas they vibrate along completely different directions. Fitting the two curves in Fig.2a at high field-strength ($E > 0.25 \times 10^8 \text{ V/m}$) to an analytical expression $\omega^2(E) + \omega^2(E = 0) = \sigma E^{\gamma}$ (derived from the Ginzburg-Landau-Devonshire theory[1]) yields, for the ω_{\parallel} and ω_{\perp} modes, an exponent γ of 0.31 and 0.56 , respectively. Our direct DFT results thus demonstrate that the exponent γ not only significantly varies from mode to mode, but also considerably deviates from the value of 0.66 from the phenomenological theory.[17]

The peculiar behavior on the field-dependence of the mode frequency in Fig.2a is found to arise from the atomic displacements and cell-shape changes induced by the electric fields, shown in Fig.2b. It can be clearly seen that below the critical E_c field the dramatic and nonlinear displacements of O atoms (with respect to Ti), as well as the sharp increase of the

c/a strain, correlate well with the phonon responses in Fig.2a. Notably, two *non*-equivalent oxygen atoms (namely, O₁ and O₃) respond remarkably similar to the applied electric field, whereas the (relative) displacement of Sr is almost negligible. These results thus show (not surprisingly) that the field effect is primarily to move Ti with respect to the rather rigid oxygen octahedral, while Sr contributes by having the “right” atomic size to form an incipient (Indeed, the low-frequency modes in Table I, which matter most for the incipient behavior, all show a significant Sr participation).

Our theoretical attempt on phonon under finite electric fields yields results that quantitatively agree with experiments. For example, besides a sharp Raman peak that results from the $\omega_{||}$ phonon, one additional peak, despite its weak intensity, was clearly observed at a lower frequency.[1] This additional peak is consistent with the existence of the ω_{\perp} mode as predicted in our calculations. Furthermore, our theoretical $\omega_{||}$ frequency at the 0.012×10^8 V/m field is determined to be 42.7 cm^{-1} , in excellent agreement with the experimental value of 45 cm^{-1} , measured under the same field strength and at temperature 8 K.[1]

Finally, we would like to examine other technological properties—namely, piezoelectric $e_{33} - e_{31}$ coefficient (which measures the piezoelectric response to a tetragonal strain when volume is preserved) and *static* dielectric ε_{33} and ε_{11} constants—of SrTiO₃ that is placed under *finite electric fields*. The $e_{33} - e_{31}$ coefficient is null at zero field (see, Fig.2a). This coefficient becomes, however, strikingly large—being as much as 19 C/m^2 under a small field of $0.012 \times 10^8 \text{ V/m}$. Note that this magnitude of piezoelectric response in SrTiO₃ (which is predicted here for the first time, to our knowledge) exceeds far more than the value of 4.08 C/m^2 in PbTiO₃[18], and even than the intrinsic theoretical e_{33} value of 9.1 C/m^2 in PMN-PT [19]. We attribute this exceptional response to the field-induced occurrence of the paraelectric-to-ferroelectric phase transition in SrTiO₃, which does not happen in PbTiO₃ and in PMN-PT. Interestingly, the $e_{33} - e_{31}$ coefficient in Fig.2a first increases, then decreases, and eventually levels off at a nonzero value of $\sim 6 \text{ C/m}^2$. Regarding the dielectric properties, the ε_{33} dielectric constant is determined to be 12215, 1120, 188, 117, 77, and 61 for the six considered field strengths at 0, 0.012, 0.22, 0.50, 1.0, and $1.5 \times 10^8 \text{ V/m}$, respectively. This tells us that the ε_{33} constant decreases dramatically by more than *one order of magnitude* when going from zero field to a very small field of $0.012 \times 10^8 \text{ V/m}$, demonstrating the existence of an incredible field-induced dielectric tunability! This giant tunability is found also true for the ε_{11} component, being 12215, 7123, 866, 485, 337, 264 at

the field strengths given above. Last (but not least), we want to point out that our direct DFT calculations of phonon frequencies and (*independently*) dielectric constants prove that the Lyddane-Sachs-Teller (LST) relationship [20] is fully valid under finite electric fields. In fact, the *static* dielectric constants obtained from direct DFPT calculations and those from the LST relationship (using phonon frequencies) are found to differ by less than 0.1%.

In summary, a practical and efficient DFT approach that allows to determine the phonon structure of solids in finite electric fields was developed, and applied, to study the electric-field effects on the zone-center modes of incipient SrTiO₃, yielding a good agreement with experiment. Our results confirm quantitatively the striking field-induced frequency shifts that have been experimentally observed—but not explained by direct first-principles theory—for nearly four decades. Our work further provides a microscopic understanding of individual phonon mode under finite fields. We also find: (i) A giant phonon hardening (as the frequency increases by *several fold* with respect to the zero-field value) takes place, not merely for the ω_{\parallel} mode that vibrates in parallel with—but also for the ω_{\perp} mode that, on the other hand, vibrates perpendicularly to—the direction of the applied electric field. (ii) After hardening, the mode showing the largest frequency shift (i.e., the ω_{\parallel} mode) has a surprisingly small Ti-atom participation. (iii) The mode at the zero-field frequency of 163.2 cm⁻¹, whereas *not* being the ongoing soft mode, displays also a remarkable response to the imposed electric field. Modes at 447 and 772 cm⁻¹ are found to be *least* affected by the **E** field. (iv) The field dependence of the soft-mode frequency exhibits a crossover at $E_c=0.5\times 10^8$ V/m—below which ω_{\parallel} and ω_{\perp} upshift sharply and nonlinearly, but differently. Above E_c , the responses of these two modes are interestingly similar with a nearly equal frequency-vs-field slope. This dependence is found to result from the field effects on atomic movements and on the tetragonal c/a strain. (v) A small electric field of 12 kV/cm is able to decrease the ε_{33} constant by one order of magnitude, showing an extraordinary dielectric tunability. (vi) An unusual piezoelectric response is predicted to exist in SrTiO₃ when placed under finite fields. We expect that the present approach will have widespread applications for determining phonon structure and dielectric tunability in solids under finite electric fields.

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FIG. 1: Mode frequency and degeneracy of SrTiO₃ under zero field (the upper panel) and under a field of 0.22×10^8 V/m (the lower panel). Zero-frequency acoustic modes are not shown. Dotted lines indicate the evolution of selected phonon modes.

FIG. 2: Dependence of (a) the ω_{\parallel} and ω_{\perp} frequencies, and (b) the z -direction displacements of Sr, O₁ and O₃ atoms (using the left vertical-axis) and the c/a strain (using the right vertical-axis), as a function of field strength. Inset in part (a) is the piezoelectric $e_{33} - e_{31}$ coefficient. In part (b), Ti is chosen as the reference for measuring the z -axis displacements of other atoms. Symbols are calculation results; lines are guide for eyes.

TABLE I: Frequency ω and mode eigenvector ξ_{τ} of the zone-center phonons in SrTiO₃ under a field of 0.22×10^8 V/m, as well as frequency shift $\Delta\omega = \omega(E) - \omega(E = 0)$. One eigenvector has three vibration components ξ_x , ξ_y and ξ_z (as specified by index τ); each component is described using the notation $\xi_{\tau} = (u_{\text{Sr}}, u_{\text{Ti}}, u_{\text{O}_1}, u_{\text{O}_2}, u_{\text{O}_3})$ with five amplitudes from Sr, Ti, O₁, O₂, and O₃ atoms, respectively. O₃ is located beneath the Ti atom. Those components not given in the table are zero. The x , y , and z -axes are, respectively, pointing along the pseudo-cubic [100], [010], and [001] directions.

ω (cm ⁻¹)	$\Delta\omega$ (cm ⁻¹)	eigenvectors
48.7	35.5	$\xi_x = (0.43, 0.27, -0.43, -0.53, -0.52)$
92.2	79.0	$\xi_z = (-0.57, -0.04, 0.51, 0.51, 0.40)$
149.9	1.2	$\xi_y = (-0.71, 0.60, 0.23, 0.16, 0.24)$
166.3	3.1	$\xi_x = (-0.58, 0.82, -0.02, -0.03, 0.01)$
189.8	26.6	$\xi_z = (-0.44, 0.86, -0.17, -0.17, -0.11)$
226.0	2.2	$\xi_y = (-0.01, 0.01, 0.71, 0.00, -0.71)$
226.4	2.6	$\xi_x = (-0.01, 0.02, 0.00, 0.70, -0.71)$
227.0	3.2	$\xi_z = (0.00, 0.00, -0.71, 0.71, 0.00)$
447.0	0.0	$\xi_y = (-0.05, -0.43, 0.59, -0.34, 0.59)$
542.3	1.2	$\xi_x = (0.04, 0.02, -0.85, 0.37, 0.37)$
549.9	8.8	$\xi_z = (0.03, 0.04, 0.36, 0.36, -0.86)$
772.4	0.6	$\xi_y = (-0.12, -0.45, 0.08, 0.88, 0.08)$



